

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 1 081 192 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.03.2001 Bulletin 2001/10

(51) Int Cl.7: C08L 83/08, C08K 5/02,
C08G 77/50

(21) Application number: 00307595.9

(22) Date of filing: 04.09.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

- Yamaguchi, Hiromasa
Matsuida-machi, Usui-gun, Gunma-ken (JP)
- Arai, Masatoshi
Matsuida-machi, Usui-gun, Gunma-ken (JP)

(30) Priority: 03.09.1999 JP 25088099

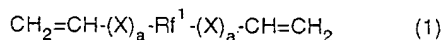
(71) Applicant: SHIN-ETSU CHEMICAL CO., LTD.
Chiyoda-ku Tokyo (JP)

(74) Representative: Stoner, Gerard Patrick et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

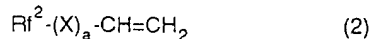
(72) Inventors:
• Fukuda, Kenichi
Matsuida-machi, Usui-gun, Gunma-ken (JP)

(54) Fluorinated curable silicone compositions

(57) A fluorinated curable composition contains as main components, (A) a linear polyfluoro compound of the formula (1):



wherein X is $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, etc., Rf^1 is a divalent perfluoroalkylene or perfluorooxyalkylene group, and "a" is 0 or 1, (B) a linear polyfluoro compound of the formula (2):



wherein X and "a" are as defined above, and Rf^2 is a monovalent perfluoroalkyl or perfluorooxyalkyl group, (C) an organosilicon compound having at least two hydrosilyl groups, (D) a platinum group catalyst, and (E) a fluorinated organopolysiloxane. The composition is vacuum deaeratable and foam breakable, cures into a gel having improved chemical and solvent resistance, and is suited for the potting, sealing and coating of electric and electronic parts.

Description

[0001] This invention relates to fluorinated curable compositions. Preferred embodiments may be effectively vacuum deaeratable and foam breakable, cure into gel products having improved chemical and solvent resistance, and be suited for the potting, sealing and coating of electric and electronic parts.

BACKGROUND

[0002] Cured gel products of silicone rubber have good electrically and thermally insulating properties, stable electric properties and flexibility. They are useful as potting and sealing compounds for electric and electronic parts, and coating compounds for protecting control circuit devices such as power transistors, ICs and capacitors from external, thermal and mechanical damages.

[0003] Typical silicone rubber composition examples forming such cured gel products are organopolysiloxane compositions of the addition curing type. The organopolysiloxane compositions of the addition curing type are known, for example, from JP-A 56-143241, 62-3959, 63-35655 and 63-33475 as comprising an organopolysiloxane having a vinyl group attached to a silicon atom and an organohydrogenpolysiloxane having a hydrogen atom attached to a silicon atom, wherein crosslinking reaction takes place in the presence of a platinum group catalyst to form a silicone gel.

[0004] However, silicon gels resulting from such organopolysiloxane compositions of the addition curing type are prone to degradation or swelling upon exposure to such chemicals as strong bases and strong acids or such solvents as toluene, alcohols and gasoline, often failing to maintain their performance.

[0005] As one solution to this problem, JP-A 11-116685 discloses a fluorochemical gel composition comprising a polyfluoro compound having two alkenyl groups and a divalent perfluoroalkylene or perfluoroalkoxyalkylene group in a molecule, an organohydrogenpolysiloxane having a hydrogen atom attached to a silicon atom, and a platinum group catalyst as well as a fluorochemical gel product resulting from curing thereof. This cured fluorochemical gel product exhibits better chemical and solvent resistance as desired than ordinary silicone gels. However, there is a drawback that when the potting compound is fed around an electric or electronic part and kept in vacuum for removing air therefrom, it can spill over the electric or electronic part package due to foaming.

[0006] It would thus be advantageous to provide a fluorinated curable composition which is effectively vacuum deaeratable and foam breakable and cures into a gel product having improved chemical and solvent resistance.

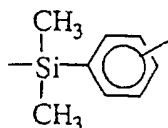
[0007] It has been found that by using a linear polyfluoro compound having at least two alkenyl groups of the following general formula (1) and another linear polyfluoro compound having one alkenyl group of the following general formula (2) as base components and formulating therewith an organosilicon compound having at least two hydrosilyl groups in a molecule, a platinum group catalyst, and a fluorinated organopolysiloxane, there is obtained a fluorinated curable composition whereof embodiments are vacuum deaeratable and foam breakable and cures into a gel product having improved chemical and solvent resistance.

[0008] Specifically, the invention provides a fluorinated curable composition comprising as main components,

(A) a linear polyfluoro compound of the following general formula (1):



wherein X is independently $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCH}_2-$ or $-\text{Y}-\text{NR}^1-\text{CO}-$ wherein Y is $-\text{CH}_2-$ or



and Rf^1 is hydrogen or a substituted or unsubstituted monovalent hydrocarbon group, Rf^1 is a divalent perfluoroalkylene or perfluoroalkoxyalkylene group, and "a" is independently equal to 0 or 1.

(B) a linear polyfluoro compound of the following general formula (2):



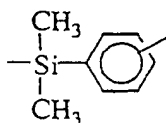
wherein X and "a" are as defined above, and Rf² is a monovalent perfluoroalkyl or perfluorooxyalkyl group,
 (C) an organosilicon compound having at least two hydrosilyl groups in a molecule,
 (D) a platinum group catalyst, and
 (E) a fluorinated organopolysiloxane.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] In the fluorinated curable composition of the invention, component (A) is a linear polyfluoro compound of the following general formula (1).



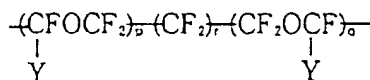
Herein X is independently -CH₂-, -CH₂O-, -CH₂OCH₂- or -Y-NR¹-CO- wherein Y is -CH₂- or



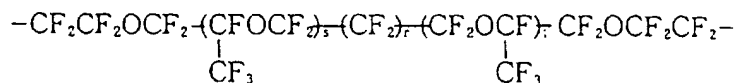
and R¹ is hydrogen or a substituted or unsubstituted monovalent hydrocarbon group. Rf¹ is a divalent perfluoroalkylene group or divalent perfluorooxyalkylene group. Letter "a" is independently equal to 0 or 1.

[0010] In formula (1), Rf¹ is a divalent perfluoroalkylene group or divalent perfluorooxyalkylene group. The preferred divalent perfluoroalkylene groups are of the formula:

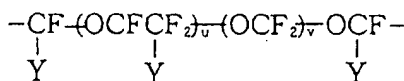
-C_mF_{2m}- wherein m is an integer of 1 to 10, preferably 2 to 6. The preferred divalent perfluorooxyalkylene or perfluoropolyether groups are of the following formulae:



wherein Y is F or CF₃, p, q and r are integers satisfying p ≥ 1, q ≥ 1, 2 ≤ p+q ≤ 200, especially 2 ≤ p+q ≤ 110, and 0 ≤ r ≤ 6;



wherein r, s and t are integers satisfying 0 ≤ r ≤ 6, s ≥ 0, t ≥ 0, 0 ≤ s+t ≤ 200, especially 2 ≤ s+t ≤ 110;

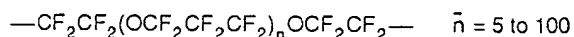
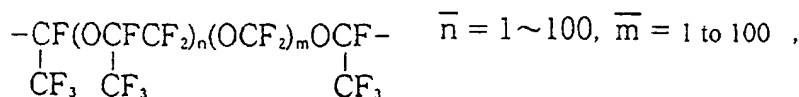
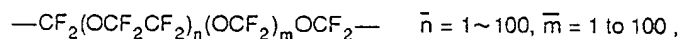
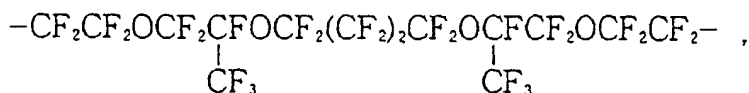
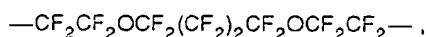
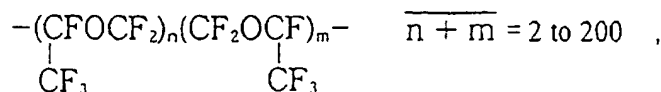
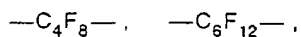


wherein Y is F or CF₃, u and v are integers satisfying 1 ≤ u ≤ 100 and 1 ≤ v ≤ 50;

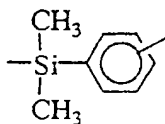


wherein w is an integer in the range of 1 ≤ w ≤ 100.

[0011] Illustrative examples of Rf¹ are given below.



[0012] In formula (1), X is independently $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCH}_2-$ or $-\text{Y}-\text{NR}^1-\text{CO}-$. Herein Y is $-\text{CH}_2-$ or a group of the following formula.



R¹ is hydrogen or a substituted or unsubstituted monovalent hydrocarbon group. The monovalent hydrocarbon groups preferably have 1 to 12 carbon atoms, more preferably 1 to 10 carbon atoms. Illustrative are unsubstituted monovalent hydrocarbon groups, for example, alkyl groups such as methyl, ethyl, propyl, butyl, hexyl, cyclohexyl and octyl, aryl groups such as phenyl and tolyl, and aralkyl groups such as benzyl and phenylethyl, and substituted monovalent hydrocarbon groups obtained by replacing some or all of the hydrogen atoms in the foregoing groups by halogen atoms such as fluorine.

[0013] The alkenyl groups in formula (1) are preferably vinyl, allyl and analogous groups having a $-\text{CH}=\text{CH}_2$ structure at the end. The alkenyl groups may be bonded to opposite ends of the backbone directly or via divalent linkage groups represented by X.

[0014] In formula (1), letter "a" is independently equal to 0 or 1.

[0015] Component (B) is a linear polyfluoro compound of the following general formula (2).

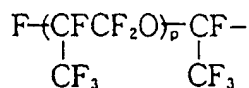


Herein X and "a" are as defined above, and Rf² is a monovalent perfluoroalkyl group or monovalent perfluorooxyalkyl group.

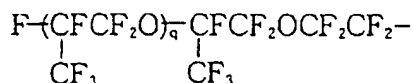
[0016] In formula (2), Rf² is a monovalent perfluoroalkyl group or monovalent perfluorooxyalkyl group. The preferred

monovalent perfluoroalkyl groups are of the formula:

$C_mF_{2m+1}-$ wherein m is an integer of 1 to 20, preferably 2 to 10. The preferred monovalent perfluorooxyalkyl or perfluoropolyether groups are of the following formulae:

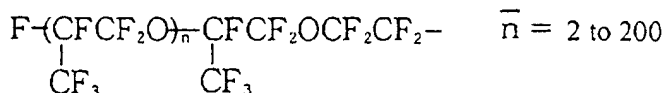
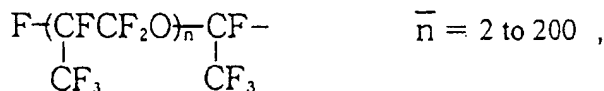


wherein p is an integer of at least 1, and



wherein q is an integer of at least 1.

[0017] Illustrative examples of R_1^2 are given below.



[0018] In formula (2), X and "a" are as defined in formula (1). It is understood that X and "a" in formula (1) may be identical with or different from X and "a" in formula (2), respectively.

[0019] Like component (A), the alkenyl group in formula (2) is preferably a vinyl, allyl or analogous group having a $-\text{CH}=\text{CH}_2$ structure at the end. The alkenyl group may be bonded to the backbone directly or via a divalent linkage group represented by X.

[0020] The composition of the invention should preferably have an appropriate flow and maintain adequate physical properties upon curing in order that the composition be used in casting, potting, coating, impregnation, adhesion or tight bonding. From this standpoint, the above-described components (A) and (B) each should desirably have a viscosity of about 5 to 100,000 centipoise (cp) at 25°C. For each component, one having an optimum viscosity within this range is selected depending on a particular application.

[0021] The mixing proportion of components (A) and (B) is not critical because the proportion largely varies depending on the desired hardness of a cured product and the structure of a crosslinker. Preferably the weight ratio of components (A)/(B) ranges from 1/100 to 100/1 and more preferably from 1/50 to 50/1.

[0022] Component (C) is an organosilicon compound which serves as a crosslinker and chain extender for both the components (A) and (B). The organosilicon compound (C) is not critical as long as it has at least two hydrosilyl groups (Si-H groups) in a molecule. When the compatibility with and dispersion in components (A) and (B) and uniformity after curing are taken into account, the organosilicon compound should preferably further contain at least one monovalent perfluorooxyalkyl, monovalent perfluoroalkyl, divalent perfluorooxyalkylene or divalent perfluoroalkylene group in the molecule as well as at least two, preferably at least three hydrosilyl (Si-H) groups in the molecule. These perfluorooxyalkyl, perfluoroalkyl, perfluorooxyalkylene and perfluoroalkylene groups are as exemplified below. monovalent perfluorooxyalkyl:

$C_mF_{2m+1}-$ wherein m is an integer of 1 to 20, preferably 2 to 10.
divalent perfluoroalkylene:

5



15



25

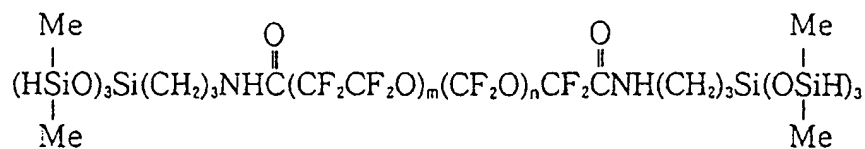
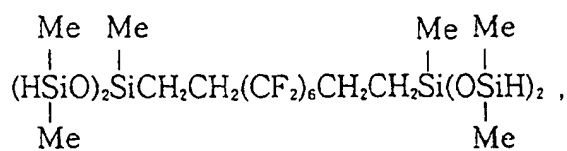


40

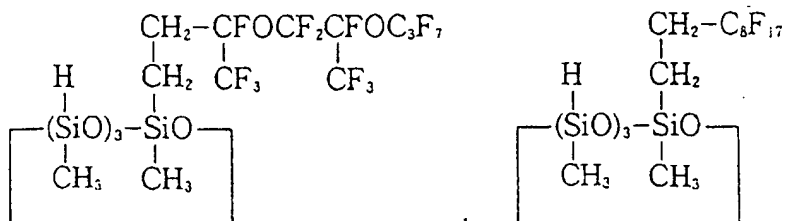
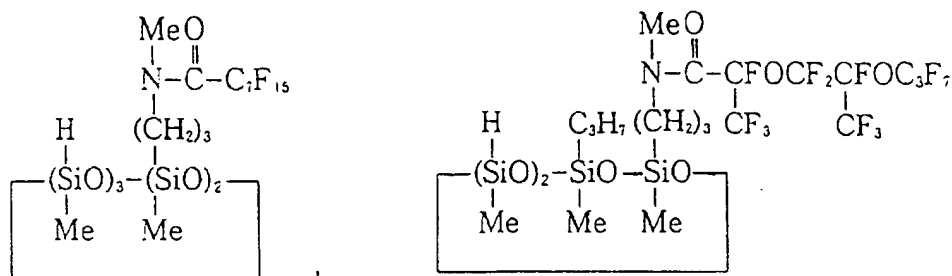
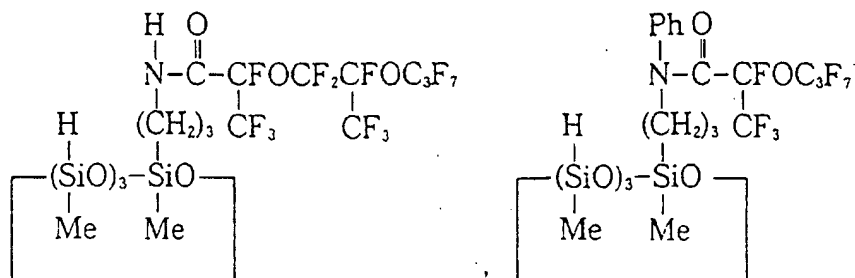
45

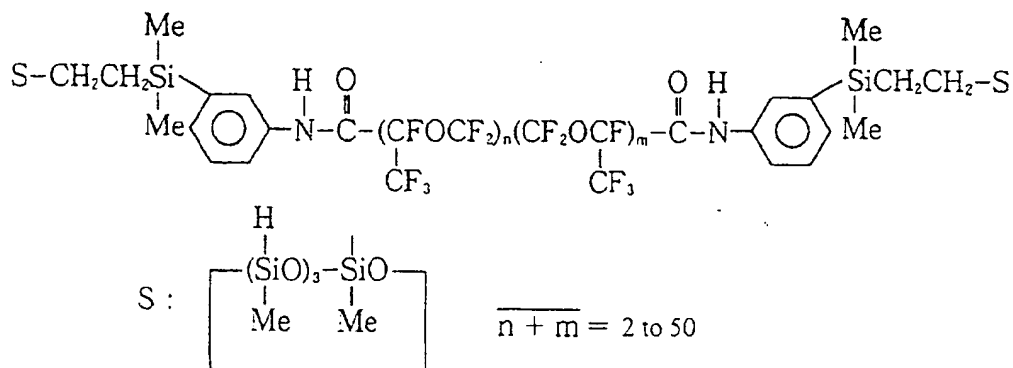
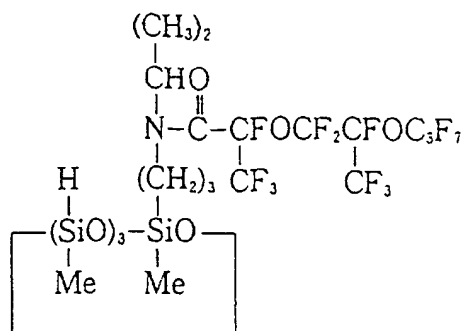
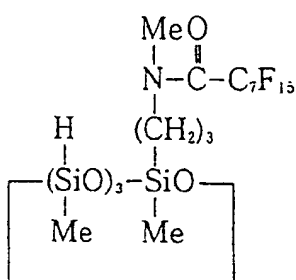
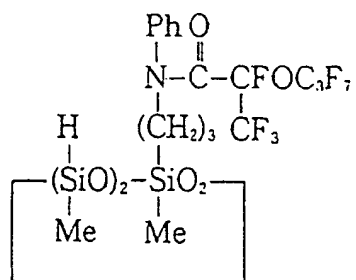
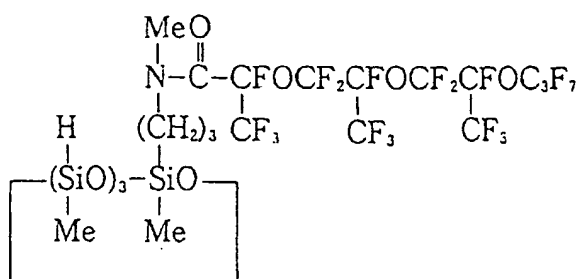
50

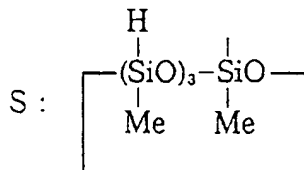
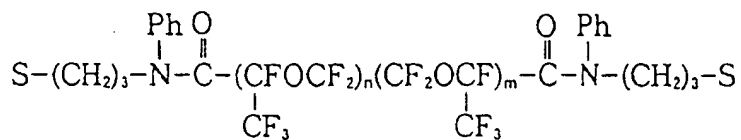




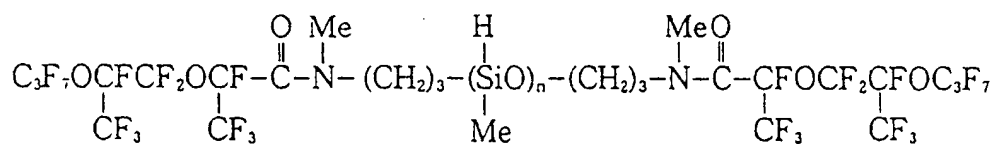
$$\bar{m} = 10, \bar{n} = 6$$



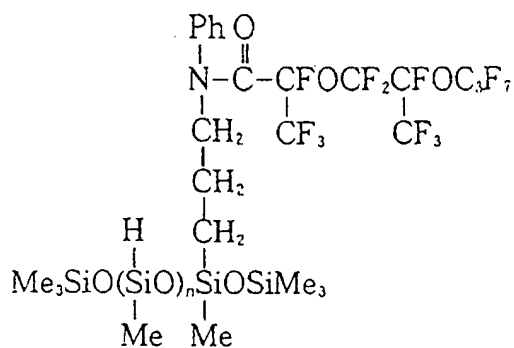




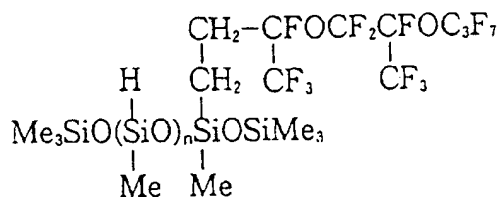
$$\overline{n + m} = 2 \text{ to } 50$$



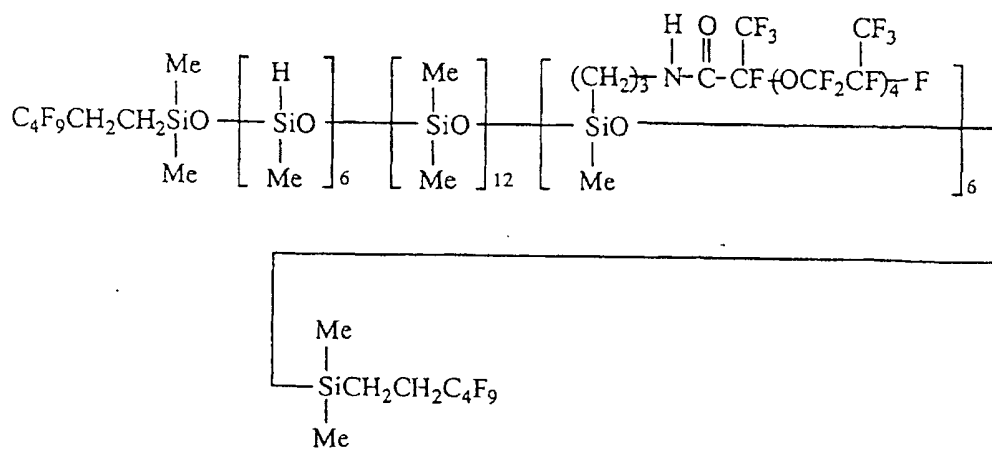
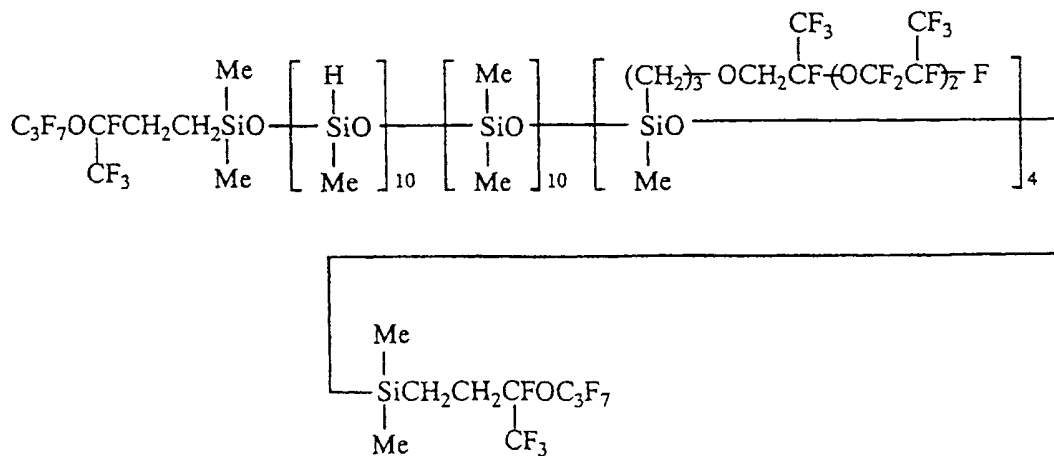
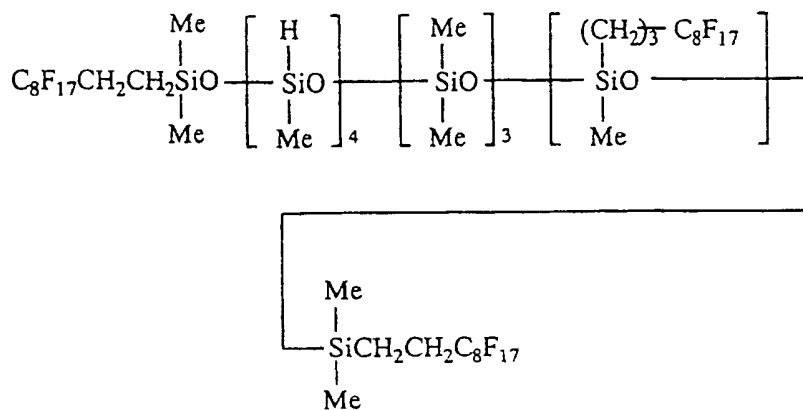
$$\overline{n} = 3 \text{ to } 50$$



$$\overline{n} = 3 \text{ to } 50$$



$$\overline{n} = 3 \text{ to } 50$$

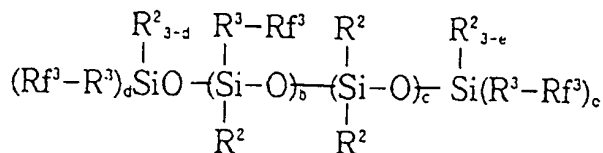




30

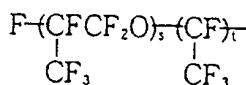
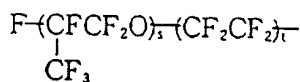


45



Herein Rf^3 is a monovalent perfluoroalkyl or perfluorooxyalkyl group of 1 to 14 carbon atoms, R^2 is independently a monovalent hydrocarbon group of 1 to 10 carbon atoms, R^3 is a divalent organic group of 2 to 5 carbon atoms, "b" and "c" each are an integer of at least 0, "d" and "e" are independently equal to 0, 1, 2 or 3, with the proviso that b, d and e are not equal to 0 at the same time.

[0033] In formula (3), Rf^3 is a perfluoroalkyl or perfluorooxyalkyl group of 1 to 14 carbon atoms, preferably 4 to 10 carbon atoms. Where two or more Rf^3 groups are included in the molecule, they may be the same or different. The preferred perfluoroalkyl groups are straight or branched ones of the formula: C_kF_{2k+1} wherein k is an integer of 1 to 14. The preferred perfluorooxyalkyl groups are straight or branches ones of the following formulae.



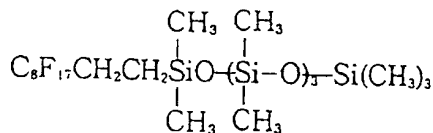
Herein, s is an integer of 1 to 4, and t is equal to 0 or 1.

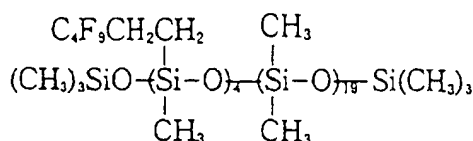
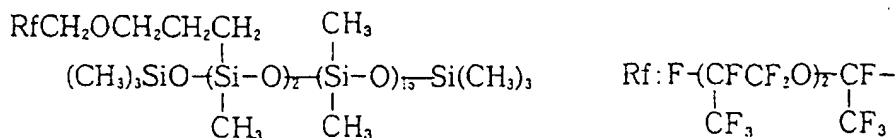
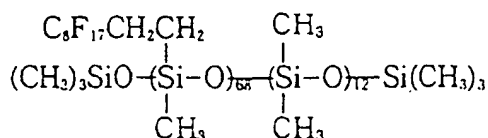
[0034] In formula (3), R^2 is independently selected from monovalent hydrocarbon groups of 1 to 10 carbon atoms, especially 1 to 8 carbon atoms. Preferred monovalent hydrocarbon groups are alkyl or aryl groups, especially methyl or phenyl.

[0035] In formula (3), R^3 is selected from divalent organic groups of 2 to 5 carbon atoms, as typified by alkylene groups of 2 to 5 carbon atoms. The alkylene groups may have at an intermediate or ends of their carbon atom chain an ether bond or an amide bond which may be unsubstituted or substituted with a C_{1-6} , especially C_{1-3} lower alkyl or phenyl. Typical examples of such alkylene groups include $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-CH_2OCH_2CH_2CH_2-$, $-CH(CH_3)-$, $-CH(CH_3)CH_2-$, $-CONHCH_2CH_2CH_2-$, $-CON(CH_3)CH_2CH_2CH_2-$, and $-CON(C_6H_5)CH_2CH_2CH_2-$. Where two or more R^3 groups are included in a molecule, they may be the same or different.

[0036] In formula (3), "b" and "c" each are an integer inclusive of 0, preferably b+c is 1 to 100, especially 2 to 60, "d" and "e" are independently equal to 0, 1, 2 or 3, with the proviso that b, d and e are not equal to 0 at the same time. It is desirable that b to d are selected such that the content of fluorine in the molecule is at least 10% by weight calculated as fluorine atoms. The fluorinated organopolysiloxane preferably has a viscosity of about 1 to 300 centistokes at 25°C.

[0037] Typical, non-limiting, examples of the fluorinated group-bearing organopolysiloxane are given below.





[0038] In the practice of the invention, component (E) should desirably have a low surface tension to components (A) and (B), specifically a surface tension of up to 30 dyn/cm, and more desirably up to 20 dyn/cm. The fluorinated organopolysiloxane having such a low surface tension (E) is effective for breaking foams. Namely, when foams evolve, component (E) having a low surface tension diffuses between an air layer and component (A) or (B) so that component (E) becomes foam-breaking nuclei.

[0039] The fluorinated group-bearing organopolysiloxane of formula (3) can be prepared by well-known methods.

[0040] Preferably the fluorinated organopolysiloxane (E) is blended in amounts of about 0.001 to 1 part, more preferably about 0.005 to 0.5 part, and most preferably about 0.005 to 0.05 part by weight per 100 parts by weight of linear polyfluoro compounds (A) and (B) combined. Less than 0.001 part of component (E) may not fully exert an anti-foaming effect. More than 1 part of component (E) may achieve no further effect and lose compatibility with components (A), (B) and (C).

[0041] In addition to the above-described components (A) to (E), the composition of the invention may further contain various additives which are per se known. Such optional components include regulators for hydrosilylation catalysts, for example, acetylene alcohols such as 1-ethynyl-1-hydroxycyclohexane, 3-methyl-1-butyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol, 3-methyl-1-penten-3-ol, and phenylbutynol, 3-methyl-3-penten-1-yne, 3,5-dimethyl-3-hexen-1-yne, etc., polymethylvinylsiloxane cyclic compounds, and organic phosphorus compounds. These regulators are effective for maintaining curing reactivity and storage stability appropriate. Other optional components include inorganic fillers, for example, fumed silica, silica aerogel, precipitated silica, ground silica, diatomaceous earth, iron oxide, zinc oxide, titanium oxide, calcium carbonate, magnesium carbonate, zinc carbonate, and carbon black. By adding such inorganic fillers to the inventive composition, the hardness and mechanical strength of cured gel can be adjusted. There may be added hollow inorganic fillers, hollow organic fillers and rubbery spherical fillers as well. The amounts of these optional components added are arbitrary insofar as they do not compromise the physical properties of cured gel.

[0042] The fluorinated curable composition comprising the essential and optional components mentioned above is cured into a gel product (or cured gel) having improved solvent resistance and chemical resistance.

[0043] By the term "cured gel" as used herein it is meant that the cured product has a three-dimensional structure in part and undergoes deformation and flow under stress. As an approximate measure, the cured gel has a hardness of up to "0" as measured by a JIS rubber hardness meter or a penetration of 1 to 200 as measured according to ASTM D-1403 (1/4 cone).

[0044] The cured gel is generally obtained by well-known methods, for example, by pouring the inventive composition of the addition curing type into a suitable mold and causing the composition to cure therein. Alternatively, the inventive composition is coated onto a suitable substrate and cured thereon. Curing is readily effected by heating at a temperature of about 60 to 150°C for about 30 to 180 minutes.

[0045] There have been described fluorinated curable compositions which are effectively vacuum deaeratable and foam breakable, and yield cured gel products having improved chemical and solvent resistance. The compositions are thus suited for the potting and sealing of electric and electronic parts and as protective coating materials for control

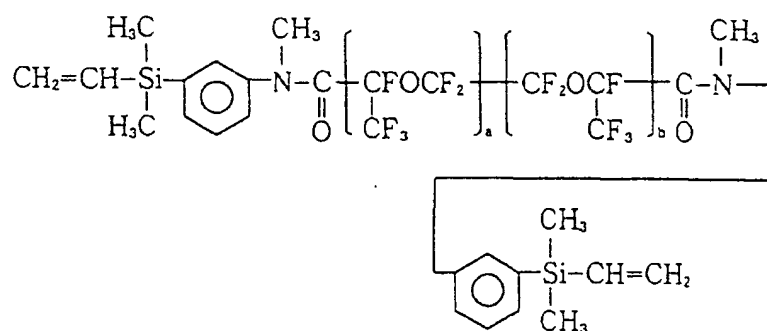
circuit elements such as power transistors, ICs and capacitors.

EXAMPLE

- 5 [0046] Examples of the invention are given below by way of illustration and not by way of limitation. Parts are by weight.

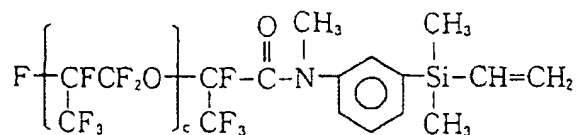
Example 1

- 10 [0047] To 50 parts of a polymer (viscosity 3,000 cp) of the following formula (4) and 50 parts of a polymer (viscosity 1,000 cp) of the following formula (5) were added 0.01 part of a compound of the following formula (6), 13.7 parts of a compound of the following formula (7), 0.15 part of a 50% toluene solution of ethynylcyclohexanol, and 0.015 part of an ethanol solution of a vinylsiloxane complex with chloroplatinic acid (platinum concentration 3.0% by weight). Mixing these components yielded a fluorinated curable composition.



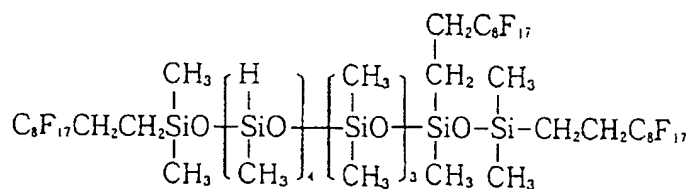
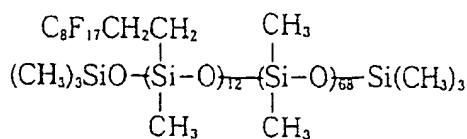
30

$$\overline{a + b} = 35$$



40

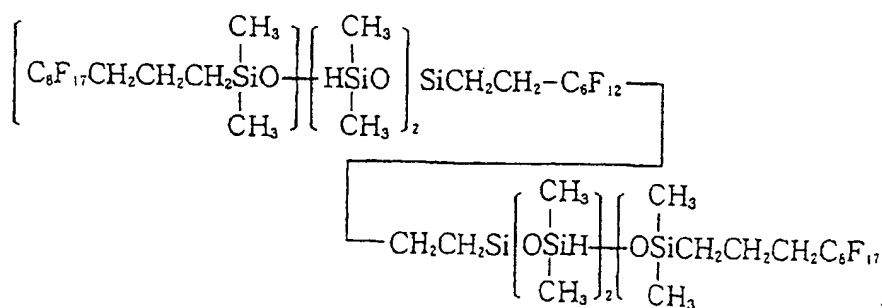
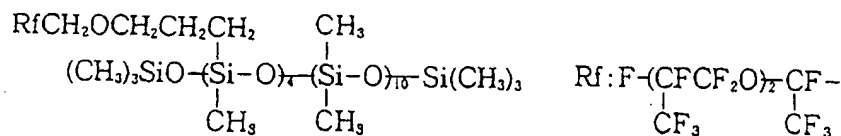
$$\overline{c} = 24$$



[0048] The composition was cured by heating at 150°C for one hour, obtaining a clear cured gel having a penetration of 78 as measured according to ASTM D-1403 (1/4 cone).

Example 2

[0049] A fluorinated curable composition was prepared as in Example 1 except that 0.03 part of a compound of the following formula (8) was used instead of the compound of formula (6) and 12.1 parts of a compound of the following formula (9) was used instead of the compound of formula (7).



[0050] The composition was cured as in Example 1, obtaining a clear cured gel having a penetration of 65.

Comparative Example 1

[0051] A similar composition was prepared as in Example 1 except that the compound of formula (6) was omitted. The composition was cured as in Example 1, obtaining a clear cured gel having a penetration of 78.

Comparative Example 2

[0052] A similar composition was prepared as in Example 2 except that the compound of formula (8) was omitted. The composition was cured as in Example 1, obtaining a clear cured gel having a penetration of 65.

[0053] Next, the above compositions were examined for anti-foaming property. Each of the four compositions, 20 ml, was admitted into a 100-ml test tube, which was shaken for one minute for foaming. After shaking, evacuation was made to a vacuum of 1 Torr. The height of foams upon foaming and the time passed until the complete extinction of foams were measured.

Table 1

	E1	E2	CE1	CE2
Foaming height (cm)	1	1	15	20
Foam extinction time (min)	0.5	0.5	10	15

[0054] Japanese Patent Application No. 11-250880 is incorporated herein by reference.

[0055] Reasonable modifications and variations are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined by the claims.

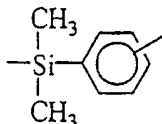
Claims

1. A fluorinated curable composition comprising as main components,

(A) a linear polyfluoro compound of the following general formula (1):



wherein X is independently $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCH}_2-$ or $-\text{Y}-\text{NR}^1-\text{CO}-$ wherein Y is $-\text{CH}_2-$ or



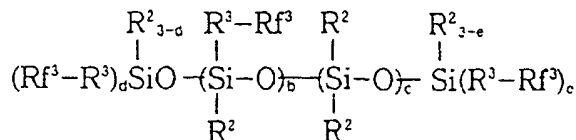
and R^1 is hydrogen or a substituted or unsubstituted monovalent hydrocarbon group, Rf^1 is a divalent perfluoroalkylene or perfluorooxyalkylene group, and "a" is independently equal to 0 or 1,

(B) a linear polyfluoro compound of the following general formula (2):



wherein X and "a" are as defined above, and Rf^2 is a monovalent perfluoroalkyl or perfluorooxyalkyl group,
 (C) an organosilicon compound having at least two hydrosilyl groups in a molecule,
 (D) a platinum group catalyst, and
 (E) a fluorinated organopolysiloxane.

2. The fluorinated curable composition of claim 1 wherein component (E) is a fluorinated organopolysiloxane of the following general formula (3):



wherein Rf^3 is a monovalent perfluoroalkyl or perfluorooxyalkyl group of 1 to 14 carbon atoms, R^2 is independently a monovalent hydrocarbon group of 1 to 10 carbon atoms, R^3 is a divalent organic group of 2 to 5 carbon atoms, "b" and "c" each are an integer of at least 0, "d" and "e" are independently equal to 0, 1, 2 or 3, with the proviso that b, d and e are not equal to 0 at the same time.

3. The fluorinated curable composition of claim 1 or claim 2 wherein 0.001 to 1 part by weight of the fluorinated organopolysiloxane (E) is blended per 100 parts by weight of components (A) and (B) combined.
4. The fluorinated curable composition of claim 1, 2 or 3 which cures into a gel product having a penetration of 1 to 200 as measured according to ASTM D-1403.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 7595

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 665 270 A (DOW CORNING TORAY SILICONE) 2 August 1995 (1995-08-02) * page 2, line 31 - line 34 * * pages 4-6, formulae * * page 7, line 43 - line 47 * * examples 1-3 *	1-4	C08L83/08 C08K5/02 C08G77/50
A	----- DATABASE HCA 'Online' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; abstract no. 102:168404, XP002154435 * abstract * & JP 59 219366 A (SHINETSU KAGAKU KOGYO KK) 10 December 1984 (1984-12-10) -----	1-4	
A	US 4 689 384 A (KONDOW KIYOHIRO ET AL) 25 August 1987 (1987-08-25) * column 5, line 21 - line 32 * * claim 1 *	1-4	
P, A	EP 0 978 526 A (ASAHI GLASS CO LTD) 9 February 2000 (2000-02-09) * page 10, line 3 - line 5 * * examples 1,2 * & WO 98 47947 A 29 October 1998 (1998-10-29) -----	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08G C08K C08L
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 1 December 2000	Examiner Hoepfner, W
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1504 (3-97) (Rev. 11-97)

BEST AVAILABLE COPY

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 00 30 7595

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

01-12-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0665270	A	02-08-1995	JP 7216092 A	15-08-1995
			DE 69509144 D	27-05-1999
			DE 69509144 T	09-09-1999
			US 5484868 A	16-01-1996
JP 59219366	A	10-12-1984	JP 1595111 C	27-12-1990
			JP 63048901 B	03-10-1988
US 4689384	A	25-08-1987	JP 1605717 C	31-05-1991
			JP 2031115 B	11-07-1990
			JP 61238851 A	24-10-1986
EP 0978526	A	09-02-2000	WO 9847947 A	29-10-1998

BEST AVAILABLE COPY